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IN-SITU TRANSMISSION ELECTRON MICROSCOPY ON OPERATING ELECTROCHEMICAL CELLS

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Solid oxide cells (SOC) have the potential of playing a significant role in the future efficient energy system scenario. In order to become widely commercially available, an improved performance and durability of the cells has to be achieved [1]. Conventional scanning and transmission SEM and TEM have been often used for ex-situ post mortem characterization of SOFCs and SOECs [2,3]. However, in order to get fundamental insight of the microstructural development of SOFC/SOEC during operation conditions in-situ studies are necessary [4]. The development of advanced TEM chips and holders makes it possible to undertake analysis during exposure to the SOFC/SOEC sample of reactive gas flow, elevated temperatures and electrical biasing in combination. This allows the study of nanostructure development under temperature and electrode polarisation conditions similar to operation conditions.

In this work, we have for the first time performed in-situ analysis of a symmetric cell inside a TEM under different configurations. In order to be able to perform in-situ experiments while drawing a current through the sample, we used a homemade TEM chip [5,6] and an 80-300kV Titan ETEM (FEI Company) equipped with an image corrector and a differential pumping system.

A symmetric cell was prepared by depositing a cell consisting of three thin films on a strontium titanate (STO) single crystal substrate by pulsed laser deposition (PLD). Lanthanum strontium cobaltite $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ (LSC) was chosen as electrode and yttria stabilized zirconia ZrO_2: 8% mol Y_2O_3 (YSZ) as electrolyte, see figure 1. High resolution TEM analysis on PLD samples after the deposition, did not reveal any second phase formation at the interface between YSZ and LSC. The in-situ experiment was firstly conducted in vacuum at temperature between 25 °C and 900 °C. Secondly, it was repeated in presence of oxygen with an oxygen partial pressure of about 2 mbar and a maximum temperature of 750 °C. Subsequently, the symmetric cell will be exposed to oxygen at 600 °C and 1 V overpotential within the ETEM. In order to do that, a symmetric cell has been placed on the chip with the use of a focus ion beam (FIB) microscope, see figure 2. To do so, a lamella was first extracted by the bulk sample and attached to a conventional TEM grid. Afterwards, the grid was tilted by 90 degrees and the lamella was detached once again and placed on the chip.

STEM-EDS investigation was used for ex-situ post mortem analysis. Finally, a bulk symmetric cell, coming from the same batch as the in-situ treated TEM samples, was tested in a furnace with similar environmental conditions. This comparison is vital for distinguishing possible surface diffusion effects caused by having a thin lamella for in-situ TEM analysis. Electrochemical properties were also investigated by electrochemical impedance spectroscopy (EIS).

In the figure 3 the cell was heat treated at 400 °C in vacuum, whereas in figure 4, the cell was treated at the same temperature but in presence of oxygen, with PO_2 of 2 mbar. Comparing the two figures, the cell exposed to oxygen showed structural changes in the LSC thin film in comparison with the sample heated in vacuum. These changes refer to the formation of grains as is confirmed by electron diffraction patterns.

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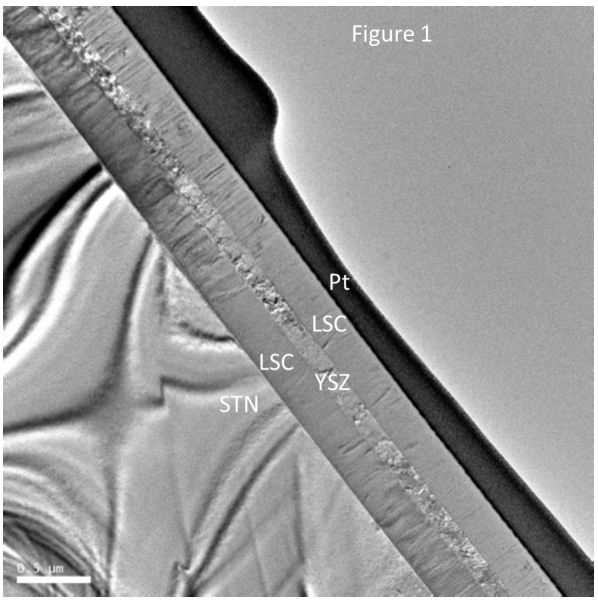
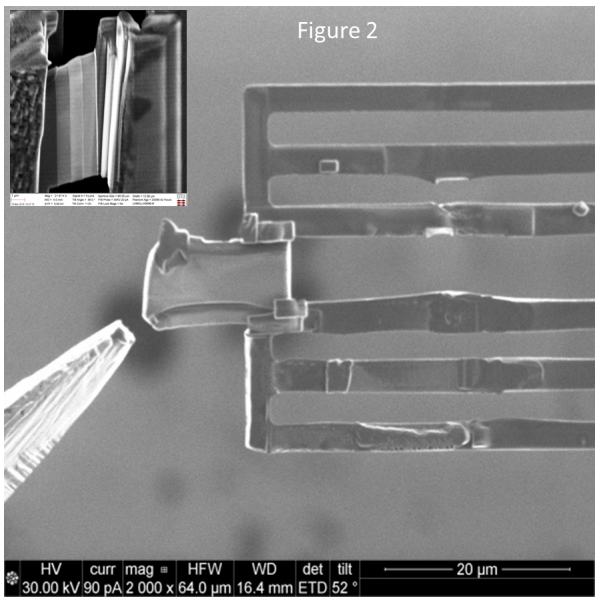
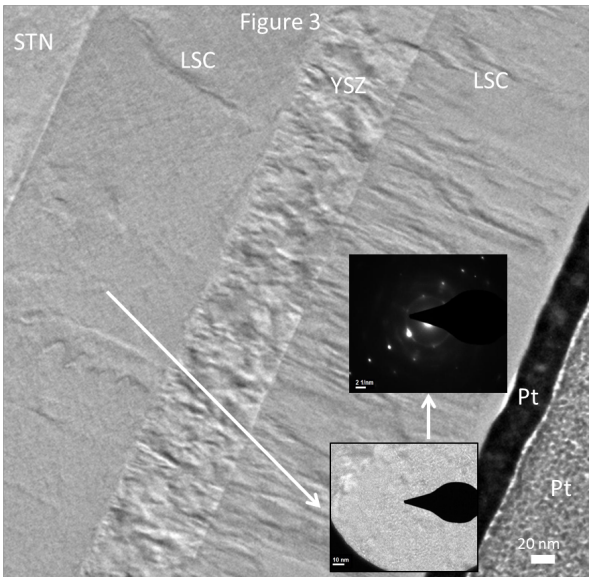


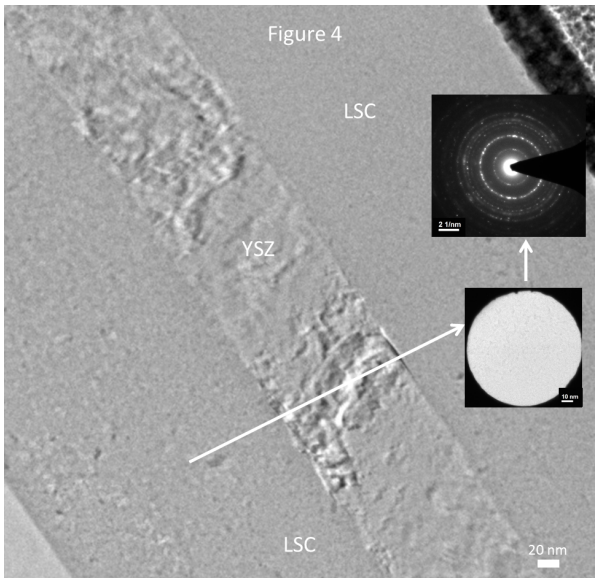
TEM image of a solid oxide symmetric cell grown by PLD on a single crystal substrate of STN.



Symmetric cell placed on a homemade TEM chip by FIB. The layers are visible in the inset, after the removing of the material re-deposition during the milling job.



TEM image of a symmetric cell exposed at 400 C in vacuum. The insets showed a higher magnification image of the LSC thin film and its equivalent diffraction pattern.



TEM image of a symmetric cell exposed to 400 C in oxygen, with PO2 = 2 mbar. LSC is polycrystalline as confirmed by the diffraction pattern made on a magnified area of the LSC thin film.